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Enthalpies of Transfer of the Alkali-Metal Poly(styrenesulfonates) from Water to Mixtures of Water and Dioxane

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ABSTRACT: Enthalpies of transfer of poly(styrenesulfonic acid) and its alkali-metal salts from water to dioxane–water mixtures containing up to 90% dioxane are reported. They were obtained from calorimetric experiments in which a dioxane–water mixture was mixed both with an aqueous polyelectrolyte solution and with water. The enthalpy of transfer does not depend on the nature of counterions; it is exothermic and its value sharply increases with the increasing content of dioxane in the binary solvent. It is shown that the electrostatic contribution to the transfer enthalpy is small compared to the chemical contribution.

Introduction

Synthetic polyelectrolytes have usually been studied in aqueous solutions,[1] and articles dealing with nonaqueous solvents or solvent mixtures, are rather scarce. In the field of solutions of simple electrolytes the most frequently used organic solvent was dioxane. It is miscible in all proportions with water, and since its dielectric constant is very low, the dioxane–water mixtures are very suitable as solvents for the study of the behavior of a solute in media of continuously and drasticly changing dielectric constant. From the point of view of any electrostatic theory the dielectric constant is the most important physical property of the solvent. It has a direct influence on the electrostatic interactions between charged particles and thus on the behavior of a charged macromolecule in solution. Therefore, studies of polyelectrolytes in solvent mixtures not only are attractive per se but should also provide an excellent test of those polyelectrolyte theories that taken into account only long-rang Coulombic forces.

One of the essential phenomena that determines the behavior of solute in a binary solvent is solvent sorting in the solvation shells of the solute, a consequence of the specific solute–solvent interactions. Changes of this preferential solvation are expected to be directly reflected in the enthalpy change accompanying the transfer of solute from an aqueous solution to a binary solvent. In this paper we describe the calorimetric procedure for obtaining the enthalpy of transfer of some alkali-metal poly(styrenesulfonates) from water to dioxane–water mixtures. From the experimental enthalpies the nonelectrostatic contribution to the transfer enthalpy due to the specific solute–solvent interactions was estimated, assuming for the electrostatic contribution the prediction derived from the cell model.[2,3]

Experimental Section

Materials. Poly(styrenesulfonic acid), HPSS, and its alkali-metal salts were all derived from one single sample of sodium poly(styrenesulfonate), NaPSS, obtained from Polysciences Inc. (Rydal, PA). According to the manufacturer's specification the NaPSS had a molecular weight of 100 000 and a degree of sulfonation of 1.00. For purification and preparation of polyelectrolyte solutions, dialysis and ion-exchange techniques were used as described in detail elsewhere.[4] The dioxane–water mixtures were prepared from distilled water and chromatographicly pure 1,4-dioxane (Riedel-De-Haen).

Apparatus. Calorimetric measurements were performed at 25 °C in an LKB 10700-2 batch microcalorimeter. Into compartments of the reaction cell 0.2 cm^3 of about 0.7 monomolar aqueous poly(styrenesulfonate) solution and 4 cm^3 of an appropriate dioxane–water mixture were pipetted. One compartment of the reference cell was filled with the amount of water equal to the water quantity in the 0.2 cm^3 of added poly(styrenesulfonate) solution and the other with 4 cm^3 of the same dioxane–water mixture. Since the two calorimetric cells are not thermally balanced (their thermal response differs by about 3.5%), a separate blank experiment had to be made for each transfer. In this experiment both cells were filled with the same amounts of water and mixed solvent as the reference cell in the main experiment. The observed thermal effect was accounted for in calculating the enthalpy of transfer, ΔH_t. In spite of this correction, the experimental error in ΔH_t is judged to be from 10% to 20%, due to the fact that the enthalpy of transfer is much smaller than the enthalpy of mixing of water and dioxane–water solvent.

The calibration of the instrument was performed by the electrical heating of the heater built in the reaction cell.

Thermodynamic Analysis

We use mathematical formalism and thermodynamic analysis similar to those of Pointud et al.[5] in their interpretation of the enthalpy of transfer of simple electrolytes

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from one solvent to another. The composition of a ternary mixture containing n_W mol of water, n_D mol of dioxane, and n_P monomol of polyelectrolyte is expressed in terms of mole ratios relative to water:

$$n_W/n_W = 1 \qquad n_D/n_W = d \qquad n_P/n_W = p$$

The enthalpy of this mixture is then

$$H(n_W,n_D,n_P) = n_W\bar{H}_W(1,d,p) + n_D\bar{H}_D(1,d,p) + n_P\bar{H}_P(1,d,p) \quad (1)$$

In the reaction cell of the calorimeter the aqueous concentrated polyelectrolyte solution, P, containing n_W mol of water and n_P monomol of polyelectrolyte is mixed with the mixed solvent, S, containing N_W mol of water and N_D mol of dioxane. The ternary mixture $M(n_W + N_W, N_D, n_P)$ is obtained accompanied with the heat effect ΔH_A

$$P(1,0,p_i) + S(1,d_i,0) \rightarrow M(1,d_f,p_f) \quad (A)$$

In the reference cell n_W mol of water, W, are mixed with the same quantity of S and the accompanying enthalpy change is ΔH_B

$$W(1,0,0) + S(1,d_i,0) \rightarrow S_f(1,d_f,0) \quad (B)$$

The quantity directly measured in the calorimeter is then $(\Delta H_A - \Delta H_B)$.

The dilution of the ternary mixture $M(n_W + N_W, N_D, n_P)$ with an appropriate amount of the mixed solvent $S_f(N_W{}^*, N_D{}^*)$ gives the enthalpy of dilution of polyelectrolyte in the mixed solvent from the concentration c_f to a reference concentration c_0, $\Delta H^S_{\text{dil}(p_f\rightarrow p_0)}$,

$$M(1,d_f,p_f) + S_f(1,d_f,0) \rightarrow M_0(1,d_f,p_0) \quad (C)$$

The corresponding enthalpy of dilution of polyelectrolyte in aqueous solution from the concentration c_i to the same reference concentration c_0, $\Delta H^W{}_{\text{dil}(p\rightarrow p_\bullet)}$, can be described by the process

$$P(1,0,p_i) + W(1,0,0) \rightarrow P_0(1,0,p_\bullet) \quad (D)$$

where the quantity of polyelectrolyte solution is the same as in process A, and the amount of water is $(N_W + N_W{}^\bullet)$ mol. For the same reference concentration of polyelectrolyte (c_0), the mole ratio of polymer to water (p) in dioxane–water mixtures (p_0) is different from that in pure water ($p_\bullet$). Evidently p_0 is continuously changing with the changing content of dioxane in the binary solvent.

The combination of the equations of type 1 for the enthalpy changes of all four processes A–D yields after lengthy algebra the following expression:

$$\Delta H_A - \Delta H_B + \Delta H^S_{\text{dil}(p_f\rightarrow p_0)} - \Delta H^W_{\text{dil}(p_i\rightarrow p_\bullet)} = (n_W + N_W + N_W{}^*)[\bar{H}_W(1,d_f,p_0) - \bar{H}_W(1,d_f,0)] + (N_D + N_D{}^*)[\bar{H}_D(1,d_f,p_0) - \bar{H}_D(1,d_f,0)] - (n_W + N_W + N_W{}^\bullet) \times [\bar{H}_W(1,0,p_\bullet) - \bar{H}_W(1,0,0)] + n_P[\bar{H}_P(1,d_f,p_0) - \bar{H}_P(1,0,p_\bullet)] \quad (2)$$

$$= \Delta H^W_{\text{dil}(p_\bullet\rightarrow 0)} - \Delta H^S_{\text{dil}(p_0\rightarrow 0)} + n_P[\bar{H}_P(1,d_f,0) - \bar{H}_P(1,0,0)] \quad (3)$$

Table I
Calorimetric Data and Enthalpies of Transfer of Some Poly(styrenesulfonates) from Water to Dioxane-Water Mixtures[a]

dioxane, wt %	$\Delta H_A - \Delta H_B$, kJ/monomol	$\Delta H_{\text{dil}}{}^S{}_{(0.0343\rightarrow 0.01)}$, J/monomol	$\Delta H_t{}^\circ$, kJ/monomol
	HPSS		
20	−2.27	−226	−1.40
40	−4.84	−192	−3.94
60	−5.72	−126	−4.75
79.7	phase separation		
80	−9.32		(−8.22)
90	−13.32		(−13.22)
	$\Delta H^W_{\text{dil}\,(0.720\rightarrow 0.01)} = -1096$ J/monomol		
	LiPSS		
20	−3.46	−200	−2.73
40	−5.20	−170	−4.44
60	−5.05	−110	−4.23
	phase separation		
80	−6.22		(−5.29)
90	−10.49		(−9.56)
	$\Delta H^W_{\text{dil}\,(0.720\rightarrow 0.01)} = -929$ J/monomol		
	NaPSS		
20	−2.36	−167	−2.36
40	−5.18	−134	−5.14
60	−4.75	−50	−4.63
61.5	phase separation		
80	−6.45		(−6.28)
90	−10.78		(−10.61)
	$\Delta H^W_{\text{dil}\,(0.720\rightarrow 0.01)} = -172$ J/monomol		
	CsPSS		
20	−1.50	−150	−1.81
40	−4.94	−120	−5.22
57.7	phase separation		
60	−4.57		(−4.73)
80	−7.88		(−8.04)
90	−10.77		(−10.93)
	$\Delta H^W_{\text{dil}\,(0.720\rightarrow 0.01)} = 160$ J/monomol		

[a] At polymer concentration of 0.01 monomol/L and 25 °C.

The first two terms on the right-hand side of eq 3 represent the enthalpies of dilution of solute in water and in mixed solvent, respectively, to infinite dilution. No reliable method for determination of these enthalpies has been proposed for polyelectrolyte solutions. Therefore, the standard enthalpy of transfer referring to the infinitely diluted state of the solute, and given by the third term of eq 3, cannot be determined. To avoid this problem, some finite concentration can be used for the reference state. Usually the lowest attainable concentration in an experiment, c_0, has been used as the reference concentration.[6] Thus, the enthalpy of transfer can be defined as

$$\Delta H_t{}^0 = \bar{H}_P(1,d,p_0) - \bar{H}_P(1,0,p_\bullet) \quad (4)$$

The first two terms on the right-hand side of eq 2 represent the relative partial enthalpy of mixed solvent, and the third term is the relative partial enthalpy of water. On the basis of the relevant enthalpy data for simple electrolytes in mixtures of water and dioxane[7] one may conclude that for low enough reference concentration c_0, these three terms almost cancel out. Anyhow, they are negligible compared to the last term on the right-had side of eq 2, which is the enthalpy of transfer, $\Delta H_t{}^0$, at polymer concentration c_0. Hence, we may write

$$\Delta H_A - \Delta H_B + \Delta H^S_{\text{dil}(p_f\rightarrow p_0)} - \Delta H^W_{\text{dil}(p_i\rightarrow p_\bullet)} \approx n_P\Delta H_t{}^0 \quad (5)$$

Results and Discussion

The experimental data and the enthalpies of transfer, $\Delta H_t{}^0$, calculated according to eq 5, for poly(styrenesulfonic acid) and some of its alkali-metal salts are given in Table I. In Figure 1 $\Delta H_t{}^0$ is plotted against the percentage of dioxane in mixed solvent. The reference concentration of the polymer is 0.01 monomol/L. The enthalpy of dilution

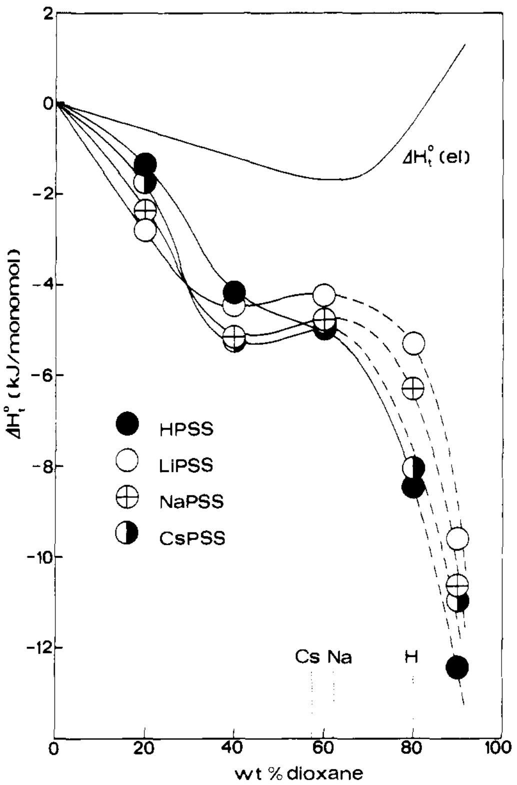

Figure 1. Enthalpy of transfer of poly(styrenesulfonic acid) and its alkali-metal salts from water to dioxane–water mixtures at the reference concentration of the polymer of 0.01 monomol/L and at 25 °C. The vertical dotted lines indicate the dioxane concentrations at which phase separation has been observed with the Cs and Na salts and with the acid, respectively. The curve denoted by ΔH_t^0(el) is the electrostatic contribution to the enthalpy of transfer predicted by the cell theory.

data needed to correct the measured enthalpy of transfer ($\Delta H_A - \Delta H_B$) were taken from our previous articles.[8-10] It has to be noted that these corrections do not considerably influence the values of ΔH_t^0 and are comparable to the absolute errors in ($\Delta H_A - \Delta H_B$) measurements. Samples are given typical mean values found with NaPSS solutions in 20%, 40%, 60%, 80%, and 90% dioxane respectively: initial percentage of dioxane 20.9%, 41.78%, 62.64%, 83.55%, and 94.05%; measured ($\Delta H_A - \Delta H_B$) −0.340, −0.576, −0.551, −0.838, and −1.157 J; blank runs 0, 0.170, 0.133, 0.0918, and 0.398 J; corrected ($\Delta H_A - \Delta H_B$) −2.36, −5.18, −4.75, −6.46, and −10.80 kJ/monomol. The latter values, given in Table I, were obtained by subtracting the blank valus from measured ($\Delta H_A - \Delta H_B$) and dividing the difference by the amount of polyelectrolyte, which was in all runs 0.000 144 monomol. Next to these data are given the enthalpies of dilution of NaPSS in 20%, 40%, and 60% dioxane, $\Delta H^{S}_{\mathrm{dil}(p_f \to p_0)}$, from the the final concentration, 0.0343 monomol/L, to the reference concentration, 0.01 monomol/L, and the enthalpy of dilution of NaPSS in pure water, $\Delta H^{W}_{\mathrm{dil}(p_i \to p_{\bullet})}$, from the initial concentration, 0.720 monomol/L, to the reference concentration, 0.01 monomol/L. The corresponding data for HPSS, LiPSS, and CsPSS are also collected in Table I together with the percentages of dioxane at which polyelectrolyte solutions separate into two clear liquid phases[11] at the final polymer concentration 0.0343 monomol/L. It has been shown previously[9] that at this critical content of dioxane in solution, $\Delta H^{S}_{\mathrm{dil}}$ tends to be zero. Therefore, only $\Delta H^{W}_{\mathrm{dil}}$ was taken into account in calculating ΔH_t in the phase separation region. Evidently in this region the enthalpy changes of other processes accompanying the phase separation add up to the enthalpy of transfer. The corresponding values of ΔH_t in Table I are therefore given in brackets.

As mentioned already in the experimental section the experimental errors are rather high, so that the observed differences between values of ΔH_t for various salts might only be apparent. Therefore, any attempt to explain these differences would be too speculative. Anyhow, the general trend of changing ΔH_t with the increasing content of dioxane in mixed solvent is the same for all the salts studied. *The transfer enthalpy first decreases with the increasing percentage of dioxane.* Between 40 and 60% dioxane it is almost constant, and it sharply decreases again in the region where poly(styrenesulfonate) solutions separate into two liquid phases.

The enthalpy of transfer can be formally considered as a sum of two parts

$$\Delta H_t^0 = \Delta H_t^0(\mathrm{el}) + \Delta H_t^0(\mathrm{st}) \tag{6}$$

where ΔH_t^0(el) is the electrostatic contribution, and ΔH_t^0(st) is the nonelectrostatic contribution. For the estimation of the electrostatic part we can use predictions from the cell model,[2,3] which has been successfully used for the theoretical interpretation of various experimental results. According to this theory, the electrostatic enthalpy of a polyelectrolyte solution, H_e, is given by the expression[8]

$$H_e = \frac{RT}{\lambda}\left[(1-\beta^2)\gamma + \ln\frac{(1-\lambda)^2-\beta^2}{1-\beta^2} + \lambda\right] \times \left(1 + \frac{\mathrm{d}\ln\epsilon}{\mathrm{d}\ln T}\right) + \frac{RT}{2\lambda}\left[1-\beta^2 - \frac{2\lambda e^{2\gamma}}{e^{2\gamma}-1}\right]\frac{\mathrm{d}\ln V}{\mathrm{d}\ln T} \tag{7}$$

where the charging parameter λ, which is the principal parameter of the cell theory, is defined by

$$\lambda = e_0^2/\epsilon kTb \tag{8}$$

In these equations β is a constant related to λ and γ, γ is the concentration parameter proportional to $-\ln c$, ϵ is the dielectric constant of the solvent, e_0 is the protonic charge, b is the length of a monomeric unit, and R, k, T, and V have their usual significance. The constant β is obtained by solving

$$\lambda = (1-\beta^2)/(1+\beta\coth\beta\gamma) \tag{9}$$

It is worth noting that β is imaginary for all values of λ applied in these calculations.[3] The contribution to the transfer enthalpy due to the polyion–counterion electrostatic interaction is then

$$\Delta H_t^0(\mathrm{el}) = H_e^0(\text{dioxane–water}) - H_e^0(\text{water}) \tag{10}$$

The calculated ΔH_t^0(el) curve is compared in Figure 1 with the observed ΔH_t^0 curves. The curve is calculated for the reference concentration 0.01 monomol/L ($\gamma = 2.9$) and temperature 298.15 K. The dielectric constant of the solvent and the temperature derivatives d ln ϵ/d ln T and d ln V/d ln T were calculated from published data as described in our recent article.[9] The calculated values at $T = 298.15$ K are as follows: ϵ = 78.48, 61.86, 44.54, 27.21, 11.86, and 6.07; λ = 2.83, 3.59, 4.99, 8.16, 18.7, and 36.6; d ln ϵ/d ln T = −1.372, −1.470, −1.674, −1.732, −1.561, and −0.124; d ln V/d ln T = 0.0768, 0.13, 0.19, 0.23, 0.30, and 0.32 for water and 20%, 40%, 60%, 80%, and 90% dioxane, respectively. In the computations the structural values of the charging parameter λ were used. As expected, the electrostatic contribution to ΔH_t is of minor importance, and the nonelectrostatic term ΔH_t^0(st), which derives largely from the effect of the solute on the structure of the solvent, is the essential factor determining ΔH_t^0. A similar situation has been observed with solutions of simple electrolytes, the nonelectrostatic part of ΔH_t exceeding the electrostatic part by an order of magnitude.[12]

The structural contribution ΔH_t^0(st) reflects specific solute–solvent interactions that are characterized by partial dehydration followed by partial dioxanation of the ions participating in the process of transferring solute from an aqueous solution to a dioxane–water mixture. Simultaneously the transfer of solute is accompanied by order-creating and order-destroying processes in the two solvents. It is well-known that the dioxane–water mixtures are less ordered than pure water and that the extent of order decreases with increasing proportion of dioxane in the mixture.[7,12,13] Furthermore, evidence exists that the large poly(styrenesufonate) anion is a structure breaker,[14] so that we may consider the alkali-metal poly(styrenesulfonates) as net structure breakers in water and in dioxane–water mixtures. Therefore, more energy must be absorbed when these polyelectrolytes are incorporated into water than when they are disolved in a mixture of dioxane and water. The enthalpy of transfer of poly(styrenesufonates) from water to this binary solvent is thus expected to be exothermic, and its absolute value should increase with the increasing content of dioxane in the mixture. The experimental observations seem to confirm such explanations.

Figure 1 shows that the enthalpy of transfer does not depend on the nature of counterions, indicating that it is primarily determined by the large, highly charged polyion. This experimental observation agrees with the recent refractometric measurements from this laboratory, which show a very similar preferential solvation of various poly(styrenesulfonates) in the binary solvent of water and dioxane.

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Effect of Entropy of Melting on Strain-Induced Crystallization

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ABSTRACT: The seemingly conflicting requirements of enhancing strain crystallization and of hampering temperature-induced crystallization can be satisfied by polymers with a low melting entropy per statistical segment. This condition is met if the entropy in the crystalline state is large. It is remarkable that this happens both with natural rubber (i.e., *cis*-1,4-polyisoprene) and with the butadiene–piperylene copolymers, due to the conformational disorder affecting the chains in spite of their parallel packing, as suggested by Corradini (*J. Polym. Sci., Polym. Symp.* **1975**, *No. 50*, 327).

Introduction

The relevance of strain-induced crystallization of stereoregular polymers to their mechanical properties is generally well recognized. It takes place during fiber spinning, film extrusion, and rubber milling, e.g., improving the processibility of the products. Also, rubberlike networks crystallize when subjected to large deformations, to advantage of their mechanical properties. It appears therefore quite reasonable that the phenomenon has been the object of a large body of experimental and theoretical studies.

Polymer networks, and particularly natural rubber networks, have usually been preferred as models for strain crystallization in view of their ability to approach thermodynamic equilibrium under well-defined conditions,[1] unlike polymer melts or solutions. The aim of the present work is to discuss some of the factors controlling crystallization of a rubber network, with a specific emphasis on the effect of the entropy of melting (s_f). As we shall see, the basic conclusion is that a small value of s_f is favorable to rubber performance, in contrast with some suggestions that it should rather be large.[2]

We shall consider separately the cases of *strain-induced* and of *temperature-induced* crystallization. As for the first item, although Flory's classical theory[1] would be quite adequate for the above-defined purpose, we shall use as a starting point the extension of that theory due to one of us, wherein the angular distribution of crystallinity in a stretched sample is obtained.[3] Our only reason for choosing the latter approach is that it appears better suited for examining the thermodynamic implications of the change undergone by the network during crystallization. In fact, let us recall that the partition function of the elastic network may be factorized into two terms: one embodies the overall elastic energy of the chains regarded as independent objects, while the other depends on the network topology and is usually neglected as being strain-invariant (see, e.g., ref 4, eq 29 and 30). However, in the particular case wherein the strain induces chain crystallization, the topology of the (amorphous) network does change. To the

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